Degradation Pathways of PCB upon Gamma Irradiation

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In order to understand the modifications of the chromatographic profile of Aroclor 1260 upon gamma irradiation, a total of 14 pure polychlorinated biphenyl (PCB) congeners were separately irradiated in solution. Dechlorination was observed, and the generated products were investigated by gas chromatography and mass spectrometry. Degradation proceeds more rapidly in methanol/water mixture than in petroleum ether, but the relative amount of *ortho*-dechlorinated congeners formed upon irradiation was smaller in the former solvent. *Ortho* chlorines are preferentially lost in petroleum ether except when they are involved in a 2,5 (or 3,6) substitution pattern, in which case *para* dechlorination becomes predominant. The precursors of some toxicologically important congeners such as congeners 77, 118, 167, and 189 have been identified. These data are useful to rationalize the modifications of the chromatographic profile of PCB complex mixture upon gamma irradiation.

Introduction

In a previous publication (*1*), the effects of gamma irradiation on Aroclor 1260 in solution were investigated. Considerable modifications of the polychlorinated biphenyl (PCB) gas chromatographic profile were observed at irradiation doses similar to the maximum recommended by the Food and Agricultural Organization of the United Nations (FAO) for food processing. Interestingly, dechlorination was the sole degradation pathway observed. Most of the congeners for which levels were enhanced upon irradiation were apparently produced through the loss of an *ortho* chlorine atom from their immediate precursor. This degradation pathway is similar to that observed for UV irradiation of PCB, a process that generates similar reaction intermediates, namely, PCB radicals (*2,3*).

However, in experiments where PCB mixtures were fortified with specific congeners, *para* dechlorination was also observed. Such a degradation pathway is barely observed upon UV irradiation of PCB containing other chlorine substituents in addition to *para* chlorines (*4*). Gamma irradiation induced generation of the 3,3',4,4'-tetrachlorobiphenyl [congener 77 according to the Ballschmiter nomenclature (*5*)] could not be studied using the Aroclor 1260 mixture because of coelution of 77 with congener 110 under the GC conditions used. This compound is one of the most toxic PCB congeners and shares many of the toxicolgical properties of the 2,3,7,8-tetrachlorodioxin (*6*). The study presented herein was designed with the objective to get further information about the degradation mechanisms of PCB upon

gamma irradiation. This approach would permit the identification of the dechlorination products that are characteristic of these congeners in the absence of interfering peaks of Aroclor complex mixtures. Finally, another objective of this study was to identify the congeners likely to generate congener 77, as its potential formation upon gamma irradiation raises toxicological concerns.

Methods

In a first step, to facilitate the analysis of the gas chromatographic (GC) and mass spectrometric (MS) data, congeners with symmetrical substitution patterns were preferentially selected. Gamma irradiation-induced degradation of such congeners should lead to the formation of a limited number of degradation products, thus facilitating the assessment of the relative reactivity of PCB congeners upon irradiation with respect to their chlorine substitution patterns.

Petroleum ether was selected as a solvent because its hydrophobicity mimics, to a certain extent, the fatty tissues in which PCB tends to accumulate in living organism. A methanol solution containing 20% water was also used to study the potential formation of PCB solvent adducts as reported upon UV (*7,8*) and gamma irradiation of chlorinated aromatics (*9*). Although such adducts were not detected in our previous experiments performed with Aroclor 1260, they could have been produced in minute amounts, preventing their positive detection and characterization from this very complex mixture upon GC analysis.

Irradiation experiments were performed with a Gammacell 220 using a Cobalt 60 source delivering 254 rad/min. The PCB congeners were dissolved in 0.5 mL of solvent at a concentration of 10 ppm and irradiated in a 1.5-mL vial closed with a screw cap. In previous Aroclor 1260 experiments (*1*), similar conditions were used, but the concentration was 4 ppm of Aroclor 1260 and the chromatographic analysis was performed using an electron capture detector.

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Gas chromatography was performed with a Varian 3500 gas chromatograph equiped with a 30 m DB-5 capillary column (0.32 mm ID, film thickness 0.25 μm) interfaced to a Finnigan Mat 800 Ion Trap Detector controlled by a IBM XT computer. The temperature programmation used was as follows: the initial temperature (70 °C) was increased up to 150 °C at 20 °C/min, then to 235 °C at 2 °C/min and finally to 320 °C at 5 °C/min.

Peak identification of the PCB congeners was performed according to Mullin et al. (10). Peak area was calculated using decachlorobiphenyl added as internal standard after irradiation. The percentage of the various congeners in the Aroclor 1260 mixture mentioned below have been reproduced from Albro et al. (11).

Results and Discussion

Degradation of Model Congeners

Table 1 displays the percentage degradation of ten model PCB congeners upon irradiation in two solvents along with the relative amounts of the various dechlorinated congeners produced. These dechlorinated congeners are grouped according to the position of the departing chlorine from their precursor. Along with these data is the percentage of chlorine atoms in this position in the starting material to be used for comparison if dechlorination was proceeding randomly. These results confirm that the solvent has an important effect on the degradation yield of these model congeners as well as on the various proportions of their degradation products. In general, higher degradation yields were obtained when irradiation was performed in the methanol/water mixture. This confirms the previous results obtained with Aroclor 1260 (1) and probably reflects the higher G values of solvated electrons generated by gamma irradiation in polar versus nonpolar solvents. These electrons react with PCB through dissociative attachment to generate a chloride anion and a PCB radical (3) that removes a hydrogen atom from the solvent to generate the dechlorinated congeners described in Table 1. Contrary to be results reported by Shimokawa et al. (9) for chlorinated aromatics irradiated in hydroxylic solvents, PCB-solvent adducts, such as hydroxy or hydroxymethyl PCB, were not detected by GC/MS.

These data also indicate that the relative amounts of the various degradation products generated upon irradiation of a specific congener are influenced by the solvent. In general the relative percentage of ortho-dechlorinated products is lower in methanol/water than in petroleum ether. This fact suggests that the •CH$_2$OH radical formed in methanol could also act as an electron donor to the PCB molecule according to a mechanism similar to that postulated by Sawai (3) for the (CH$_3$)$_2$ •COH radical. Dechlorination at the more hindered ortho position would then be impeded, whereas the formation of meta- and para-dechlorinated products would proportionally be favored. This specific property of ortho-substituted PCB in methanol/water is best illustrated by congener 54, the sole compound investigated in this study to bear only ortho chlorines. Indeed, the degradation yield of this compound is only 34%, while congener 77, which bears

no ortho substituent, is 59% degraded (Table 1).

The relative amounts of ortho-dechlorinated products formed upon irradiation vary considerably from one congener to another. Whereas congeners 47, 136, and 155 are largely degraded and most of their degradation products are obtained through ortho dechlorination in both solvents, congeners 52, 153, and 194 undergo little degradation (15, 15, and 25%, respectively) in petroleum ether. In this solvent and in methanol/water, although much more degradation takes place, the relative amount of ortho-dechlorinated products is small relative to para- or meta-dechlorinated products. In the latter case, these three congeners have their ortho chlorines involved in a 2,5 (or 3,6) substitution pattern that apparently reduces dechlorination at this position. This is even more evident for congeners 200 and 136. These two congeners have an ortho chlorine involved in a 2,5 substitution pattern and another ortho chlorine without para chlorine substituent. In both cases the degradation yields are high and proceed to a very large extent through loss of the ortho chlorine without a para substituent.

Sawai et al. (12) also observed a reduction in reactivity for chlorines involved in a 2,5 (or 3,6) substitution pattern upon gamma dechlorination of pentachlorobenzene in organic solvent. The most abundant degradation product is 1,2,4,5-tetrachlorobenzene generated through the loss of the C-3 chlorine, the only one without para chlorine substituent. They also reported that 1,2,3,5-tetrachlorobenzene was more degraded than the symmetrical 1,2,4,5-tetrachlorobenzene in which all the chlorines have a para substituent. Finally, 85% of the degradation products of 1,2,3,5-tetrachlorobenzene is 1,2,4-trichlorobenzene, the remaining 15% being the corresponding 1,3,5 isomer. The favored formation of the 1,2,4 isomer is again explained by the greater susceptibility to radiation-induced dechlorination of chlorine atoms without para chlorine substituent. This reduced reactivity might be caused by a reduced affinity for electrons of the chlorine substituent in such substitution pattern. Similar results were also observed by Sugimoto et al. (13) upon electrochemical reduction of hexachlorobenzene in organic solvent.

At the relatively low radiation dose used (1.25 Mrad), mono-dechlorinated products are almost exclusively generated, but some degradation products resulting from the loss of two chlorines were also observed. Their formation provides useful information about the degradation pathways of PCB congeners substituted with an odd number of chlorines. In all the cases where di-dechlorinated products were unequivocally identified, the second dechlorination always occurred on the most substituted ring of the mono-dechlorinated intermediate. In two cases, the identity of the di-dechlorinated products could not be assessed because two congeners that could be produced from the starting material have similar retention times.

First, congener 155 can ultimately generate the symmetrical 2,2', 4,4' congener 47 through ortho dechlorination of the very abundant 2,2',4,4',6 intermediate congener 100, or the 2,4,4',6 congener 75 could be generated through ortho dechlorination of the less chlorinated ring of the same 2,2',4,4',6 penta-chlorinated precursor. The retention times

Table 1. Degradation products of pure PCB isomers upon 1.25 Mrad in organic solvents.

Starting material	% Destruction of starting material		Isomers produced via ortho dechlorination	% Produced[b]		% o-Cl[c]	Isomers produced via meta dechlorination	% Produced		% m-Cl[c]	Isomers produced via para dechlorination	% Produced		% p-Cl[c]	Isomers produced from loss of 2 Cl from the starting material
	Methanol	Pet ether[a]		Methanol	Pet ether			Methanol	Pet ether			Methanol	Ether		
(209)[d]	58	54	2,2',3,3',4,4', 5,5',6 (206)	9	ND[e]	40	2,2',3,3',4,4', 5,6,6' (207)	35	35	40	2,2',3,3',4,5, 5',6,6' (208)	56	65	20	ND
(200)	60	42	2,2',3,4',5,5',6 (187) and 2,2', 3,3',4,5',6 (175)	22 / 19	42 / 10	12 / 25	2,2',3,4',5,6,6' (188) and 2,2', 3,3',4,6,6' (176)	14 / 15	6 / 8	12 / 12	2,2',3,3',5,6,6' (179)	27	33	12	2,2',3,3',4,6 (131) –o from (176)
(194)	47	15	2,3,3',4,4',5,5' (189)	4	29	25	2,2',3,4,4',5,5' (180) and 2,2',3,3',4,4',5 (170)	29 / 6	18 / ND	25 / 25	2,2',3,3',4,5,5' (172)	60	53	25	ND
(136)	51	56	2,2',3,5',6 (95) 2,2',3,3',6 (84)	82 / ND	52 / 12	33 / 33	2,2',3,6,6' (96)	18	36	33	NR[f]	NR	NR	NR	2,2',5,5' (52) –o from (95)
(155)	49	51	2,2',4,4',6 (100)	81	83	67	NR	NR	NR	NR	2,2',4,6,6' (104)	19	17	33	2,2',4,4' (47) –o from (100) or 2,4,4',6 (75) –o from (104)
(153)	46	15	2,3',4,4',5 (118)	3	27	33	2,2',4,4' (99)	7	ND	33	2,2',4,5,5' (101)	90	73	33	2,2',5,5' (52) –p from 101
(54)	34	59	2,2',6 (19)	100	100	100	NR	NR	NR	NR	NR	NR	NR	NR	2,6 (10) –o from 19 or 2,2' (4) –o from 19
(52)	40	25	2,3',5 (26)	100	100	50	ND	ND	ND	50	NR	NR	NR	NR	3,3' (11) –o from 26
(47)	46	59	2,4,4' (28)	76	94	50	NR	NR	NR	NR	2,2',4 (17)	24	6	50	4,4' (15) –o from (28)
(77)	59	18	NR	NR	NR	NR	3,4,4 (37)	ND	24	50	3,3,4' (35)	100	76	50	3,3' (11) –o from (35)

[a] Petroleum ether.
[b] Percentage of the total area of monodichlorinated compounds.
[c] Percentage of ortho, meta, or para substituents in the starting material.
[d] Numbers in parentheses are congener numbers.
[e] ND, not detected.
[f] NR, not relevant.

Table 2. Degradation of pure PCB isomers upon 1.25 Mrad irradiation in petroleum ether.

Starting material	% Destruction	Isomers produced via *ortho* dechlorination	% Produced[a]	Isomers produced via *meta* dechlorination	% Produced	Isomers produced via *para* dechlorination	% Produced
(180)[b]	28	2,3',4,4',5,5' (167)	45	2,2',4,4',5,5' (153)	22	2,2',3,4',5,5' (146)	33
(138)	45	2,3',4,4',5 (118) 2,3,3',4,4' (105)	88 3	ND[c]	ND	2,2',3',4,5 (97) 2,2',3,4,5' (87)	5 4
(118)	45	3,3',4,4' (77)	75	ND	ND	2,3',4',5 (70)	25
(101)	20	2,3',4',5 (70)	32	2,2',4,5' (49)	3	2,2',5,5' (52)	65

[a]Percentage of the total area of monodechlorinated isomers.
[b]Congener number in parentheses.
[c]ND, not detected.

of 47 and 75 are similar and, although the 2,2',4,4',6 intermediate congener 100 bears two reactive *ortho* chlorines on its most substituted ring, some *ortho* dechlorination of the less chlorinated ring cannot be excluded.

In the other case, congener 54 generated the 2,2',6 congener 19, which could be the precursor of two other congeners with almost identical retention times, the 2,2' congener 4 and the 2,6 congener 10. They could arise from the loss of an *ortho* chlorine from the most and the less substituted ring, respectively, of congener 19. However, as in the previous case, the presence of two reactive *ortho* substituents in the most substituted ring of congener 19 does not favor dechlorination of its less substituted ring.

Degradation of Congeners Present in Aroclor 1260

Because only two of the ten congeners shown in Table 1 are present in significant amounts in Aroclor 1260, namely, congeners 194 and 153, irradiation was repeated in petroleum ether with four other congeners that are present in large amounts in this PCB mixture (Table 2). These congeners, namely, congeners 180, 138, 118, and 110, are not symmetrical, and three of them are substituted with an odd number of chlorines. They were selected to further verify the observed reactivity toward gamma-induced dechlorination at the various positions of the biphenyl nucleus for unsymmetrical and/or odd numbered substituted congeners. They are also potential precursors of the toxicologically important coplanar congeners 77 and 189 and of the mono-*ortho*-substituted congeners 118 and 167. These latter four congeners share many of the toxicological properties of 2,3,7,8-tetrachlorodioxin (TCDD) (14). The data from Table 2 will be discussed along with the relevant data from Table 1 (congener 194 and 153) to rationalize the results previously obtained from the gama degradation of Aroclor 1260 (1). In this experiment, the variation in the GC peak area of selected congeners was observed before and after irradiation at 1.25 Mrad of a 4 ppm solution of Aroclor 1260 in petroleum ether. This experiment was performed to mimic the behavior of PCB contaminants in the nonpolar lipidic matrix of food treated with gamma irradiation. These results are sum-

Table 3. Effects of 1.25 Mrad on selected isomers of Aroclor 1260 in petroleum ether.[a]

Isomer number	% Variation	Isomer number	% Variation	Isomer number	% Variation
201	-32	180	-13	123[b]	+320
199	-39	177	-37	118	+540
194	-17	167	+258	110/77	-5
189	+43	146	+87	70	+1500
185	-30	128	-49		
183	-23	126	+14		

[a]Relative to the area of the peak of the unirradiated solution.
[b]Relative to peak area at 250 krad.

marized in Table 3.

The 2,2',3,3',4,4',5,5' congener 194 is a precursor of the toxicologically important 2,3,3',4,4',5,5' congener 189. In petroleum ether congener 194 is only degraded to a small extent because of the presence of a 2,5 substitution pattern (Table 1). Interestingly, the percent degradation of congener 194 is similar no matter if the irradiation is performed on a 10 ppm solution of the pure congener or on a 4 ppm solution of Aroclor 1260. The increase of congener 189 as observed in Table 3 can be explained by the degradation of its precursor 194 because 189 represents 30% of the degradation products arising from the degradation of 194 (Table 2). Congeners 194 and 189 account for 2.2% and 0.13% of Aroclor 1260, respectively.

Congener 180 is moderately degraded (28%) in petroleum ether because both of its rings bear 2,5 substitution patterns that deactivate its *ortho* chlorines (Table 2). In the Aroclor experiment, congener 180 decreased only by 13%. This difference can be accounted for by the concomitant formation of 180 through *meta* dechlorination of 194 (Table 1) as well as from the potential *ortho* dechlorination of the 2,2',3,3',4,4',5,6 congener 196 (0.79% of Aroclor 1260). It was observed (Table 2) that the toxicologically important 2,3,4,4',5,5' congener 167 accounts for 45% of the degradation products of 180. This reaction could explain the large increase of 167 shown in Table 3. Congeners 180 and 167 account for 7.2% and 0.17%, respectively, of Aroclor 1260. Congener 180 is also one of the precursor of the 2,2',3,4',5,5' congener 146, which also increased considerably in the Aroclor experiment (Table 3).

The 2,2′,3,4,4′,5′ congener 138 is considerably degraded (45%) in petroleum ether, mostly through the loss of the *ortho* chlorine of the 2,3,4 substituted ring to generate the toxicologically important congener 118 (Table 2). The other *ortho* chlorine is in a 2,5 substitution pattern, and only a very small amount of congener 105 is produced by dechlorination at this position. The 540% increase of 118 in the Aroclor experiment (Table 3) can be explained by the former degradation pathway, taking into account that congener 138 is very abundant in Aroclor 1260 (5.0%). Congener 153 (8.2% of Aroclor 1260) also contributes to this large increase of 118, although it is much less degraded than 138 in petroleum ether (Table 1).

Congener 118 is 45% degraded in petroleum ether, and its main degradation product (75%) is the toxic 3,3′,4,4′ congener 77, as shown in Table 2. In the Aroclor experiment congener 77 cannot be resolved from the co-eluting congener 110 under the chromatographic conditions used, and the resulting peak did not vary significantly upon irradiation, as shown in Table 3. Because congener 118 is predominantly degraded into congener 77 and because 118 accounts for 2.0% of Aroclor 1260, the amount of congener 77 in the irradiated mixture certainly increased. The absence of any significant variations in the 110/77 peak area is probably due to concommitant degradation of 110. The most substituted ring of 110 bears a 2,3,6 substitution pattern, and congener 136, which shares a similar substitution pattern, is 56% degraded in petroleum ether, as shown in Table 1. Congener 77 accounts for only 0.04% of Aroclor 1260 and is only degraded to a small extent (18%) upon irradiation in petroleum ether (Table 1). Finally, congener 118 is also a precursor of the 2,3′,4′,5 congener 70 (Table 2). The large percent degradation of a congener such as 118 that bears a 2,5 substitution pattern on its more substituted ring is probably due to the fact that congener 118 bears only one *ortho* chlorine. The loss of this chlorine atom would be energetically favored because it would promote the formation of a coplanar and stabilized radical intermediate.

Finally, Table 2 shows that congener 101, a precursor of congener 70, is only degraded to a small extent in petroleum ether (20%) because of the 2,5 substitution pattern on both rings. In the Aroclor 1260 experiment, the amount of congener 70 increased by 15-fold (Table 3). Congener 101 and 70 accounts, respectively, for 5.0% and 0.85% of Aroclor 1260. The other potential precursors of congener 70, in addition to congener 118 mentioned previously, are congeners 110 and 87, which account for 3.57 and 1.1% of Aroclor 1260. These data could explain the large increase of congener 70, as shown in Table 3.

Conclusion

The degradation pathways of PCB congeners upon gamma irradiation were investigated. The reactivity of the chlorines at various positions decreases in the order *ortho* > *para*

> *meta*, except when all the *ortho* chlorines are involved in a 2,5 or 3,6 substitution pattern, in which case *para* dechlorination becomes much more important. When odd-numbered substituted biphenyls are degraded, dechlorination occurs on the more substituted ring. The precursors of the toxic congeners 77, 118, 167, and 189 have been identified. These observations are useful to understand the modifications of the profile of PCB mixtures upon gamma irradiation.

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